Emulsion Polymerization of Acrylic Esters and Other Vinyl Monomers

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The previously reported study of emulsion polymerization of acrylic esters was extended. It was demonstrated that many types of latex containing various acrylic polymers and copolymers can be prepared and that the emulsifying system has a profound effect on their properties. Emulsions containing 60% resin were prepared satisfactorily. The emulsifying systems and conditions developed for acrylic esters, which differ in several respects from those recommended for dienes, are suitable for the polymerization of certain other vinyl-type monomers.

A STUDY of the preparation of resin emulsions or dispersions from certain monomeric alkyl acrylates and the effect of various ingredients in the emulsion was reported previously (13). This study was extended because of the importance of resin emulsions as such in several applications and the fact that emulsion polymerization affords a convenient method for converting monomer into polymer. In the study reported here, attention was directed toward (a) use of additional types of emulsifiers, (b) preparation of high-solids latices by direct polymerization, (c) preparation of 2-chloroallyl alcohol copolymers in high- and low-solids latices, (d) polymerization and copolymerization of the higher alkyl acrylates, (e) use of various organic peroxides as polymerization initiators, (f) continuous polymerization, and (g) use of emulsifying systems found to be suitable for acrylates in the polymerization of certain other vinyl monomers. Because of the possibility that acrylic esters might hydrolyze during the emulsion polymerization and yield polymers or copolymers of acrylic acid, the resistance of certain alkyl acrylates to hydrolysis under appropriate experimental conditions was investigated briefly. The observations made in studying these several points are concerned with several factors that are important in determining the properties of resin emulsions (4, 19). These factors include the constitution of the film absorbed around the dispersed particles, the nature and particle size of the dispersed phase, solids concentration, pH, and relative specific gravities of the two phases.

EXPERIMENTAL

The procedure most frequently used in this laboratory for the routine preparation of a wide variety of polymers and copolymers is described below. Since the same procedure was used also to prepare the emulsions of the present work (except when otherwise indicated) a detailed account of the method is given.

	Parts by Weight
Water	200
Triton 720 (based on monomer)[a]	0.5 to 1
Tergitol paste No. 4 (based on monomer)	1 to 2
Monomer (ethyl acrylate)	100
Ammonium persulfate (sufficient to produce polymerization at refluxing temperatures)	0.005

[a] Chemical nature of emulsifying agents used is given in Table II.

Water and the water-soluble ingredients were charged into a round-bottomed, three-necked, ground-glass joint flask fitted with a stirrer, reflux condenser, and thermometer well. The solution was stirred with anchor, paddle, or half-moon-type stirrers at 50 to 150 r.p.m. The monomer and any remaining ingredients were then added, and the flask was heated until refluxing occurred. Flasks ranging in size from 200 ml. to 12 liters were used, and were generally filled to 60% capacity. Heat was applied intermittently, if needed, to induce polymerization. If the polymerization did not start within 10 minutes after refluxing first occurred, additional ammonium persulfate was added. If excessive quantities of catalyst were required, the monomer was not considered to be of the proper purity. The reaction usually proceeded at a rate sufficient to cause refluxing without external heating for 15 to 30 minutes without flooding the condenser. Heat was then applied, and the refluxing temperature raised to 93° to 95° C. for completion. The emulsion was then steam distilled for 15 to 30 minutes. To obtain the polymer, the hot emulsion was run slowly into twice its volume of hot (approximately 90° C.), rapidly stirred 3 to 5% sodium chloride solution. The precipitated polymer in the form of discrete particles was washed with hot water until free of salt and dried. Polymers prepared in this manner were soluble in organic solvents such as toluene, benzene, ethyl acetate, acetone, and dioxane, whereas those made with substantially larger amounts of catalyst were not. If the emulsion itself was desired, it was cooled and poured into storage vessels.

Some polymerization initiators are capable of cross-linking soluble polymeric alkyl acrylates (12). It is of interest to compare the proportion of persulfate used by the authors with the larger quantities (approximately 1%) employed by other workers (19) in the copolymerization of butadiene with various vinyl monomers.

Redistilled monomers were used and in general precautions previously described (19) regarding elimination of detrimental impurities were observed.

In the present report, low- and high-solids refer to emulsions containing 30 to 45% and 45 to 60% internal phase, respectively. The percentage of total solids was determined by evaporating volatile matter from a known quantity of emulsion.

TABLE I. SAPONIFICATION OF ACRYLIC ESTERS AT ROOM TEMPERATURE[a]

Experiment No.	Total Normal NaOH Added, Ml.	Total Time Elapsed, Min.	pH
1	1	0	10
		18 hr.	10
2	0	0	6
	2	1	6
	5	2	7
	10	3	7.5
	20	5	9
	20	7	7.5
	30	8	9
	30	10	7
	50	11	10
	50	13	7
	100	15	10
	100	17	8
	175	18	10
	175	20	7
	0	0	6
	1	1	9
	1	3	8
	1	5	7
	5	8	10
	5	11	7
	10	12	10
	10	16	7
	30	58	10
	30	62	8
	100	67	10
	100	72	8
	200	100	10
	200	104	10
	200	105	9
	200	107	7

[a] Experiment 1, water, 350 ml.; Triton 720, 3 g. Experiment 2, methyl acrylate, 150 g.; water, 600 ml. Triton 720, 3 g. Experiment 3, ethyl acrylate, 150 g.; water, 350 ml.; Triton 720, 3 g.

SAPONIFICATION OF ACRYLIC ESTERS

Inasmuch as acrylic esters (23) hydrolyze with moderate ease in solution under alkaline conditions and fatty acid soap solutions, frequently used as emulsifiers, have a pH of approximately 10, a brief study was made of the hydrolysis of emulsions of methyl and ethyl acrylate.

It was found that emulsified acrylic esters are hydrolyzed rapidly under alkaline conditions at room temperature, whereas hydrolysis under neutral conditions is relatively slow even at refluxing temperatures. Ratchford and Faucette (14) of this laboratory have observed that essentially neutral emulsions of ethyl acrylate hydrolyze at a negligible rate (0.35% in 6 hours at 70° C.). The first experiment of Table I shows that the pH of the mixture of water, emulsifier, and sodium hydroxide remains constant at 10. The second and third experiments (Table I) show that the pH drops rapidly to 7 upon the addition of sodium hydroxide to monomeric methyl or ethyl acrylate emulsions, indicating rapid formation of sodium acrylate and neutralization of the sodium hydroxide.

The saponification experiments (Table I) show that the pH should be below 7 during emulsion polymerization of acrylic esters if a polymer or copolymer free of salts of acrylic acid is desired. Alkaline materials, however, may be added before or during the polymerizations. When sodium hydroxide is added, for example, partial or total neutralization occurs, with the formation of monomeric or polymeric sodium acrylate. The presence of the latter and sodium acrylate copolymers improves the emulsion stability. As alkyl polyacrylates are substantially resistant to hydrolysis (1), alkaline conditions can be maintained after polymerization is complete.

EFFECT OF THE EMULSIFIER

In studying the effect of emulsifiers it was convenient to use the classification of emulsifying agents given by Sutheim (20) and Bennett (2). Most of the emulsifiers used have been described and listed in the technical literature (2, 4, 6, 7, 20-22). When identical or similar commercial products were available under different trade names, no attempt was made to compare or evaluate different brands. Therefore, the use of particular brands does not

Fatty acid soaps (Class 1a), used in large quantities in the preparation of GR-S and other elastomers, are most effective as emulsifiers at a pH of approximately 10 and lose much of the efficiency in hot water (20). In view of the loss of effectiveness of the soaps at elevated temperature and the facile saponification of acrylic esters (Table I), it was predicted that alkali metal soaps would be poor emulsifiers for acrylic esters.

This prediction was generally supported by experiment, but it was found possible to prepare soap emulsions of acrylic esters by adding alkali at regular intervals during the polymerization. The resulting emulsions were of low stability, however, and a considerable amount of polymer precipitated during polymerization (Table II). Although commercial soaps and a hydrogenated soap specially prepared for polymerization were used, the study did not include metallic soaps (Class 1b). (The sample, obtained from the Oil and Fat Division of this laboratory, was a selectively hydrogenated tallow soap: iodine No., 31.8; total polyunsaturated acids, 0.33%.)

Amine salts of fatty acids (Class 2) would be expected to be more promising than the sodium salts because of their recognized emulsifying efficiency and lower pH (approximately 8). The amine soaps, however, required excessive amounts of catalyst and yielded polymers of decreased molecular weight. This finding is in harmony with the known antioxidant and inhibiting effects of amines (5, 8, 10).

Sulfated compounds (Class 3) emulsified ethyl acrylate readily and formed moderately good low-solids emulsions (less than 45% internal phase). The sodium salts of sulfated castor oil (Aquasol AR 75%) and of sulfated alcohols yielded satisfactory low-solids emulsions when used alone, and were used in conjunction with other emulsifiers to prepare good high-solids emulsions. Films made from Aquasol AR 75% emulsions were clear and nearly colorless. Hydrolysis of sulfated emulsifiers appeared to be negligible or unimportant, possibly because the time required to perform the emulsion polymerization was only 1 or 2 hours.

The use of sulfonate salts (Class 4) yielded good emulsions that were stable during preparation and storage. It was observed again in these experiments that single agents were not so useful as suitable mixtures. Very good samples were prepared with single emulsifiers, however, with practically no precipitation during polymerization or steam distillation (Table II). Because petroleum sulfonates are relatively inexpensive, several of these were tried and found to be satisfactory. Emulsifiers of Class 3 and 4 appear to be generally useful when the sole purpose of the emulsion polymerization is to convert monomer into polymer, and a high-solids emulsion is not required.

Aromatic sulfonates (or the mixed alkyl-aryl types) were found to be useful emulsifying agents. They are especially advantageous when used in combinations to make high-solids latices. Owing to the wide variations in structure in this type of emulsifier, a more careful selection must be made to obtain the proper balance of hydrophobic and hydrophylic properties. Also, this class offers greater possibilities of finding agents for specific effects and for emulsifying different monomers. For example, the condensation product of a naphthalenesulfonic acid and formaldehyde (Darvan No. 1, Triton R-100, or Daxad No. 11), which is a dispersing agent and does not appreciably lower surface tension, may be used in small amounts to improve emulsions made with Triton 720, an aryl-alkyl ether sulfonate.

Cationic agents (Class 5) may be used in the emulsion polymerization of ethyl acrylate. When cetyldimethylbenzylammonium chloride (Triton K-60) was used (Table II), some coagulation (approximately 0.5%) generally took place, but the remaining emulsion was very stable on standing. In general, this class does not appear to be so good as the two preceding ones.

Nonionic agents (Class 6) were also tried, glyceryl monostearate being used the most, in conjunction with other agents—mostly sulfonated materials. Several other members of this class were used, alone or with other agents, with little or no success. Diethylene glycol monolaurate (Glaurin), glyceryl mono-oleate, condensation products (Emulphor O, AG, ELA), Spans, and Tweens, were all used without success in the reflux emulsion polymerization. Perhaps additional study is warranted with other members of the nine classes of nonionic surface active agents listed by Goldsmith (9).

Natural agents (Class 7)—for example, alginates, caseinates, pectinates, lecithin, starch derivatives, and gum tragacanth—were used with other materials in preparing acrylic emulsions (13). They may be added as compounding ingredients, alone or with other agents. In general they are not sufficient as emulsifiers when used alone, but act as stabilizing agents in conjunction with other materials. Stabilizing agents may be very useful in practical application where it is desired to apply the latex by

TABLE II. SINGLE EMULSIFIERS USED IN EMULSION POLYMERIZATION OF ETHYL ACRYLATE

Experiment No.	Trade name	Chemical name	Class	% Based on monomer	Monomer Used, %	(NH₄)₂S₂O₈, %	Total Solids, %	Total Precipitate, %	Viscosity, Centipoises[a]	Remarks[b]
E-256[c]	...	Sodium stearate	1a	4.0	33	0.002	..	...	..	Large globule of polymer precipitated during polymerization
E-239	...	Soap[d]	1a	5.0	33	0.011	..	...	..	Large globule of polymer precipitated during polymerization
E-265	...	Soap[d], buffer soln.[e]	1a	4.0	33	0.880	..	...	..	Coagulation took place during polymerization
C-109[f]	...	Monoamylamine oleate	2	3.8	38		..	...	..	A sirupy mass separated out during polymerization
M-330	Aquasol AR 75%	Sulfated castor oil	3a	4.0	50	0.016	48.5	2.1	225	Good emulsion, fine particle size
M-313	Aquasol AR 75%	Sulfated castor oil	3a	3.0	33	0.017	33.5	2.0	4	Good emulsion, fine particle size
M-191	Duponol ME	Sodium alkyl sulfates, principally lauryl	3b	1.5	43	0.005	42.5	0.5	36	Good emulsion, fine particle size
M-192	Duponol ME	Sodium alkyl sulfates, principally lauryl	3b	3.0	43	0.005	46.3	0.5	108	Good emulsion, fine particle size
E-35[f]	Tergitol penetrant No. 4	Sodium 2-methyl-7-ethylundecyl-4-sulfate	3b	2.0	33	0.001				Good emulsion, fine particle size
M-305	Surfax W O	Highly sulfated fatty ester	3b	5.0	50	0.005	34.0	0.95	5	Good emulsion, fine particle size
M-306	Surfax W O	Highly sulfated fatty ester	3b	5.0	50	0.010	46.0	1.1		Good emulsion, fine particle size
M-1	Petronate H L	Petroleum mahogany sulfate	4a	4.5	33	0.005		Very slight	Low	Good emulsion, fine particle size
M-3	Atlantic Refining Co. No. 52446	Water-soluble sulfonate	4a	2.5	33	0.005		2.0	Low	Emulsion broke on standing overnight
M-4	Atlantic Refining Co. No. 52445	Oil-soluble sulfonate	4a	2.5	33	0.005		Moderate	Rather thick	Good emulsion
M-5	Petromix 5A	Petroleum mahogany sulfonate, 25% oil	4a	2.0	43	0.010		0.2		Good emulsion, fine particle size
N-29[g]	Acto 550-W	Water-soluble petroleum sulfonate	4a	5.0	33	0.010		0.07	Low	Good emulsion, fine particle size
M-46[g]	Acto 550-W	Water-soluble petroleum sulfonate	4a	1.25	33	0.010		2.0	Low	Good emulsion, fine particle size
M-69[g]	Acto 1000-W	Purified petroleum sulfonate	4a	2.5	33	0.005		1.5	3	Good emulsion, fine particle size
M-68	Ultrawet A	Petroleum sulfonate	4a	3.0	33	0.015		12.5	Low	Good emulsion, fine particle size
M-362	Irepon T gel	Sulfonated ethylmethyloleyl amide	4b	0.75	33	0.002		...	Low	Good emulsion, fine particle size
E-38[h]	Triton 720	Alkyl-aryl ether sulfonate	4b	2.22	45	0.011	40.0	9.8		Good emulsion, fine particle size
M-297	Triton 720	Alkyl-aryl ether sulfonate	4b	3.0	33	0.037	32.0	9.8		Good emulsion, fine particle size
M-307	Surfax T R	Alkyl naphthalene sulfonate	4b	4.6	33					Polymer separated from emulsion
A-9[i]	Aerosol OS	Sodium alkyl naphthalene sulfonate	4b	3.0	50					Good emulsion, fine particle size
A-80[i]	Aerosol OT	Dioctyl sodium sulfosuccinate	4b	3.0	35	0.015	34.4	0.09	10	Good emulsion, fine particle size
M-384	Santomerse D	Decylbenzene sodium sulfonate	4b	3.0	33	0.015	32.6	0.14	5	Good emulsion, fine particle size
M-385	Santomerse 3	Dodecylbenzene sodium sulfonate	4b	3.0	33	0.05		11.3	3	Good emulsion, fine particle size
M-361	Unitex	Alkylated aromatic sulfonate, sodium salt	4b	3.0	33	0.05	34.5	0.5	2400	Good emulsion, fine particle size
N-154[h]	Triton K-60	Cetyldimethylbenzylammonium chloride	5		28	0.026		Considerable	Low	Poor emulsion, lumps
R-14	Armac 18D	Octadecylamine acetate	6	1.7	43	0.120		Large		Very poor emulsion
E-13[k]	Glaurin	Diethylene glycol monolaurate	6	2.5	33	0.015		Large		Very poor emulsion
C-131[h,j]	Kessco 26207	Dodecaethylene glycol monolaurate	6	1.3	33			Large		Very poor emulsion
M-225	Kessco 26207	Polyglycol ester	6	2.5	17	0.020		16	Low	Good emulsion, fine particle size
M-220	P.R. 1180F	Polyglycol ester	...	...	5.4	0.008		7	Low	Good emulsion, fine particle size
M-96[k]	P.R. 1180F	None	...	...	33	0.012			Low	Good emulsion, fine particle size
M-52[k]	P.R. 1180F	None	...	...	33	0.010	9.8	Large	Low	Good emulsion, fine particle size
M-312	P.R. 1180F	None	...	...	33					

[a] Emulsion viscosities were measured with a Brookfield Synchro-Lectric viscometer at 12 r.p.m. at room temperature.
[b] Emulsions were judged to be of good quality if they were smooth, exhibited no visible lack of homogeneity, and were stable after standing for several months; fine particle size means that practically all the particles were smaller than 0.5 micron.
[c] Sodium stearate formed in situ; pH dropped from 9 to 7 even though 0.28% NaOH was added in portions during polymerization.
[d] A selectively hydrogenated tallow soap; iodine number, 31.8; total polyunsaturated acids, 0.33%.
[e] Clark and Lubs buffer solution (pH 8.6) used instead of water; emulsion remained alkaline during run.
[f] Methyl acrylate monomer used; 40 ml. of 3% hydrogen peroxide and 3 g. of benzoyl peroxide used for each 100 g. of monomer.
[g] Emulsifying agent calculated as 50% solid.
[h] Emulsifying agent calculated as 30% solid.
[i] Methyl acrylate plus 10% acrylonitrile monomers and 0.5% benzoyl peroxide used.
[j] Methyl acrylate monomer used and 0.75% of 30% H₂O₂.
[k] Methyl acrylate monomer used.
[l] 23 ml. of H₂O₂ (30%) and 0.67 g. of benzoyl peroxide used per 100 g. of monomer.

calendering, spraying, brushing, dipping, or passing through squeeze rolls. The viscosity may also be increased by these protective colloids for the purpose of increasing the amount of rubber or polymer deposited per dip or pass through the machine.

The viscosity of high-viscosity, high-solids emulsions may be reduced by the addition of certain agents. Thus it becomes apparent that the viscosity and the solids content of these latices may be varied independently and at will within certain limits.

Finely divided solids (Class 8) such as bentonite clays were also used as auxiliary agents in preparing emulsions, without any apparent advantage.

In connection with the study of emulsifiers, preparation of acrylic emulsions without added emulsifying agents is of interest. In these experiments, traces of ammonium persulfate were added to initiate polymerization, but the quantity used could not have exerted an appreciable emulsifying effect. Low-solids emulsions were obtained, and there was always a large amount of coagulation during the run (Table II, Experiments M-52, 96, and 312). The resulting emulsions, however, were moderately stable. Persulfates have been used also by Renfrew and Gates (17) to prepare emulsions.

All the emulsions described above were the low-solids type—that is, they contained less than 45% internal or resin phase. This type of emulsion is useful for several purposes. Most of the commercial synthetic rubber has been made in low-solids emulsion (18). Some applications to cloth or leather require dilute emulsions, even as low as 5%. Several of the systems described above are suitable for the emulsion polymerization

TABLE III. PREPARATION OF HIGH-SOLIDS POLYETHYL ACRYLATE EMULSIONS

Experiment No.	Triton R-100, %	Glyceryl Monostearate, %	Triton 720ᵃ, %	Ethyl Acrylate Monomer, %	Ammonium Persulfate, %	Total Solids, %	Total Precipitate, %	Brookfield Emulsion Viscosity, Centipoises, 12 R.P.M.
M-83	0.5	..	3.0	55	0.0045	46.0	0.05	100
M-94	1.0	..	2.0	55	0.0045	54.7	0.22	85
M-84	1.0	..	3.0	55	0.0045	..	0.07	..
M-95	1.0	..	4.0	55	0.0045	50.7	0.03	38
M-124	1.5	..	1.5	55	0.0045	..	0.13	..
M-123	1.5	..	2.0	55	0.0045	48.6	0.06	30
M-337b	2.0	..	2.0	60	0.2200	54.6	0.30	52
M-331b	1.0	..	2.0	55	0.1200	50.9	0.43	60
N-111c	1.4	2.4	1.5	60	0.0830	56.5	2.1	Very thick
N-157d	1.0	1.5	1.5	45	0.0110	44	0.4	15
N-133e	1.2	1.0	0.9	55	0.0166	49.5	4.7	70
N-140f	1.0	1.0	0.9	50	0.0133	44	1.8	15
N-184d	1.0	1.5	1.5	45	0.0100	45	0.66	32
M-326g	1.0	1.0	1.5	55	0.0910	51	1.5	53
M-328g	1.0	1.5	2.0	55	0.0910	52	0.2	90
M-329b	1.0	1.5	2.0	55	0.1210	51	1.0	55
M-380f	..	1.0	1.0	50	0.0333	50	0.65	850
M-317h	..	1.5	0.15	55	0.0227	46	1.75	210
N-137f	..	1.0	0.9	50	0.0100	49.1	1.6	335
M-332f	..	1.5	1.0	55	0.0136	51	2.9	740
N-135f	..	1.0	..	50	0.0100	49.5	4.3	145
N-138	0.5	1.0	..	50	0.0100	51	2.2	50
N-145h	..	1.5	..	50	0.0133	49.5	1.5	575

Experiment No.	Tergitol Penetrant No. 4, %ⁱ	Acto 550-W %ʲ	Triton 720ᵃ, %	Ethyl Acrylate Monomer, %	Ammonium Persulfate, %	Total Solids, %	Total Precipitate, %	Brookfield Emulsion Viscosity, Centipoises, 12 R.P.M.
M-185	1.0	..	1.3	43	0.0243	43.0	0.45	10
M-28	0.6	..	0.4	55	0.0045	..	Very large	..
M-26	0.3	..	0.6	55	0.0048	..	Broke on cooling	..
N-155	1.5	..	1.5	45	0.0063	45.0	0.13	..
N-158	1.5	..	1.5	45	0.0063	43.0	0.20	..
N-183	1.5	..	1.5	45	0.0047	42.0	0.60	..
M-323f	..	..	1.0	55	0.0136	48.0	4.9	20
M-115	..	2.0	0.5	40	0.0083	42.3	0.17	153
M-76	..	3.8	2.3	55	0.0045	40.5	7.6	20
M-90k	..	..	3.0	55	0.0045	49.5	0.06	10
M-114l	..	..	0.6	40	0.0083	..	0.08	32
M-91m	..	..	3.0	55	0.0045	..	0.06	..
M-64n	..	..	0.5	50	0.0066	50.2	0.06	48
M-182	2.0	2.0	..	43	0.0050	38.0	0.60	10
M-181	1.0	2.0	..	43	0.0050	40.0	1.2	12

ᵃ Calculated as 30% emulsifying agent.
ᵇ Also 1.5% Permasol Base.
ᶜ Also 0.8% Duponol ME.
ᵈ Also 1.0% Duponol ME.
ᵉ Also 3.0% Surfax W. O.
ᶠ Also 3% Aquasol AR 75%.
ᵍ Also 1% Permasol Base.
ʰ Also 4% Aquasol AR 75%.
ⁱ Calculated as 25% emulsifying agent.
ʲ Calculated as 50% emulsifying agent.
ᵏ Also 1% Daxad No. 11.
ˡ Also 2.1% Acto 1000 W.
ᵐ Also 1% Darvan No. 1.
ⁿ Also 3.3% Ultrawet A.

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of acrylic esters, and yield satisfactory and stable emulsions. Although stable emulsions were obtained in some instances with a single emulsifier, it was generally preferable to use two or more agents.

Emulsifying agents that allow precipitation or produce emulsions that break on standing are noted in Table II. In all instances where good emulsions of fine particle size were produced, the effect of storage was negligible; some emulsions (depending on the date made) have stood for 5 years.

Mechanical tests, such as those run with a Hamilton-Beach soda fountain mixer, are generally unsatisfactory for testing synthetic latices (including those of the present study) because of foaming and the fact that synthetic latices are more stable to mechanical agitation than natural rubber latex.

Stability to rubbing and to friction is imparted by the incorporation of protective colloids or similar materials after the emulsion has been prepared, and therefore this subject could be investigated appropriately in connection with compounding studies. As far as the authors know, none of the emulsifying agents used as such does much to promote frictional stability in these or in other synthetic latices. Emulsions having excellent stability to friction can be made by the incorporation of 0.5% or more of a suitable agent, such as modified casein and alginic acid derivatives. These agents may be added before or during the polymerization (13).

Chemical stability of the emulsion can be predicted moderately well from a consideration of the chemical nature of the emulsifying agents—for example, the addition of acids to soap emulsions would be expected to break the emulsion. It has been pointed out that emulsions made with Triton 720 are stable to electrolytes. Dilution stability of the good emulsions described in this paper was excellent. The emulsions were obviously stable to boiling, for they were steam distilled in their preparation. They were stable also at the freezing point of water (the added materials lowered the freezing point).

PREPARATION OF HIGH-SOLIDS EMULSIONS

The advantages and applications of high-solids emulsions (50 to 60% resin), discussed earlier for other polymers (3), include high production of resin for any given plant, decreased cost of storage and transportation, and deposition of larger quantities of resin in one operation. Moreover, high-solids emulsions can be diluted satisfactorily when a low-solids latex is desired. Production of high-solids latices from natural rubber latices by various concentration techniques has been a common practice for some time. In view of the obvious advantages of avoiding concentration operations, considerable attention has been given to the direct preparation of synthetic high-solids emulsions. Direct preparation of high-solids emulsions presents problems (such as viscosity peak during polymerization, greater heat evolution, maintaining latex stability, and foaming) not experienced with low-solids emulsions (3, 19). The high-solids acrylic emulsions of the present work were prepared by the general technique described in the experimental section.

During the search for suitable emulsifiers and conditions, it was considered that a satisfactory high-solids emulsion should meet the following specifications: solids content of 50 to 60%, preferably more than 55%; small particle size with no agglomeration; lack of coagulation during the polymerization and subsequent handling; polymerization time of 1 to 2 hours; high polymerization yield; adaptability to the preparation of a wide variety of polymers and copolymers; long storage life without creaming;

TABLE IV. PREPARATION OF ETHYL ACRYLATE-CHLOROALLYL ALCOHOL COPOLYMERS

Experiment No.	Triton 720a, %	Acto 550-Wb, %	Alkanol S, %	Triton R-100, %	Permasol Base, %	Total Monomer, %	2-Chloroallyl Alcohol %	Total Solids, %	Total Precipitate, %	Brookfield Emulsion Viscosity, Centipoises, 12 R.P.M.	pH of Finished Emulsion
M-353	2.5	..	..	..	..	33	5	26	4.0	4	2
M-367	..	3.5	..	..	..	33	5	27.5	4.2	3	2
M-365	..	3.0	..	..	..	33	5	17	1.2	3	2
M-364	1.5	1.5	..	..	..	33	5	27	7.5	3	3
M-381	3.5	..	1.0	..	..	60	5	57	4.7	148	2
M-382c	3.5	..	1.0	..	..	60	5	55	0.45	360	7
M-383c	3.5	..	1.5	..	..	60	5	52	0.3	150	7
M-355	3.0	..	0.5	..	..	33	5	27	4.2	4	2
M-377c	3.5	..	..	1.0	..	60	5	53	0.06	72	7
M-378c	3.5	..	..	1.0	..	60	10	50	0.04	22	7
M-375c	3.5	..	..	1.0	..	60	5	57	0.10	360	7
M-340	2.5	..	..	1.0	1.5	60	5	56	0.01	60	2
M-342	2.5	..	..	1.0	1.5	60	5	54	0.01	110	2
M-346	3.0	..	..	1.0	1.5	60	5	54	0	80	2
M-338	2.5	..	..	1.0	1.5	60	5	54	0	90	2
M-386d	..	..	..	..	..	52	5	45	2.1	218	2
M-266e	0.5	..	..	1.4	..	55	5	54	0.45	100	2
M-296f	0.9	..	..	1.5	1.5	60	5	61	0	..	2

a Calculated as 28% emulsifying agent.
b Calculated as 50% emulsifying agent.
c Ammonia was used to keep the pH above 5.
d 2.0% Santomerse 3, 2% Aquasol AR 75%, and 1% glyceryl monostearate used.
e 1.5% glyceryl monostearate, and 0.75% Duponol ME also used.
f 1.5% glyceryl monostearate also used.

and facile preparation and operation on a larger scale. In addition, the viscosity, pH, and chemical and heat stability should be satisfactory.

Preparation of acrylic resin emulsions containing 50 to 60% resin by direct polymerization required more emulsifying agents, the concentration of primary and auxiliary emulsifying agents usually being 2 or 3% of the monomer. Since the choice and proportions of these two allow the most latitude in experimental work, many combinations were tried (Table III). Triton 720 (sodium salt of aryl-alkyl polyether sulfonate) or a mixture of Triton 720 and Acto 550-W (water-soluble petroleum sulfonate) was found to be satisfactory in preparing emulsions of higher resin content and promoting smooth reaction with little precoagulation in the polymerization vessel.

Preparation of the acrylic high-solids emulsions was like the preparation of previously described butadiene copolymer emulsions (3), in that a viscosity peak occurred. It was observed that the viscosity peak involved in the polymerization of acrylic esters can be satisfactorily reduced by the use of Triton R-100, Daxad No. 11, or Darvan No. 1. The amount of these agents needed (0.5 to 2%) was determined by the viscosity desired.

In preparing high-solids latices, two or more of the following types of agents were always used: primary emulsifying agent; viscosity reducing agent; antifoaming or foam-reducing agent; auxiliary-emulsifying agent; pH-controlling agent; and stabilizing agent or agents (natural colloids).

It was not necessary to use special agitation or to increase the reaction time beyond the 1- or 2-hour period generally used for the emulsion polymerization of acrylic esters.

Little or no trouble with foaming was experienced during polymerization with most of the systems used. In several instances, steam distillation of the residual monomer (2 to 5%) was retarded or made very difficult because of foaming. Capryl alcohol, Dow Corning antifoam A, or Adhesive Products foam reducer 1917 was used in these cases, with varying degrees of success.

The system was kept neutral or acid. Agents were chosen so that the system would remain stable as the pH decreased during polymerization. In many instances the pH of the finished latex was as low as 2 or 3. To regulate the pH, ammonia, ammonium carbonate, Clark and Lubs' buffer mixtures, MacIlvaine's buffer mixtures, disodium phosphate, or Permasol Base (a mixture of low titer soap, fatty acids, and a water-soluble solvent) were used. Stabilizing agents—that is, natural colloids—were used in some cases.

The most troublesome problem was the prevention of partial coagulation in the reaction flask during polymerization and subsequent steam distillation. This premature coagulation was normally small, 0.1 to 1.0%, but its elimination was a problem. In several experiments this was accomplished (Tables III and IV). These systems employed a total of approximately 4 or 5% of emulsifying or regulating ingredients, as compared with the 1 to 3% used with low-solids emulsions. Recipes of the type given in Tables III and IV have been used satisfactorily on a larger scale (10-gallon glass-lined vessel) by W. W. Howerton and his associates in the Chemical Engineering and Development Division of this laboratory.

PREPARATION OF 2-CHLOROALLYL ALCOHOL COPOLYMERS

A study was made (Table IV) of the preparation of 2-chloroallyl alcohol copolymers because preliminary data indicated that such copolymers vulcanize at a relatively high rate (11). Owing to the greater acidity developed in the preparation of chloroallyl alcohol copolymers, a more stringent test was put upon the emulsifying systems. Triton 720 and Acto 550-W, used either alone or together, were not satisfactory (compare with Table II). By keeping the pH above 5 with intermittent additions of ammonia, the amount of precipitation was minimized and the solids content increased. Permasol Base greatly retarded the rate of reduction of pH during polymerization, and although the final pH was low, the amount of precoagulation was kept at a minimum. Additional catalyst was required in making the chloroallyl alcohol copolymers, and this produced a softer material. Some of the copolymers from high-solids emulsions were insoluble in toluene.

HIGHER ALKYL ACRYLATES

Another series of emulsions of theoretical and practical interest is that of the higher n-alkyl polyacrylates. Methyl acrylate may be polymerized readily in emulsion, and several agents have been used for this purpose (13). The reaction is rapid, even violent at times, and must be conducted under prescribed conditions. The polymer is tough, nontacky, and lacking in resilience. Its appearance depends to a great extent upon the molecular weight; a soft, flexible material is obtained under conditions that yield polymers of low molecular weight. Ethyl acrylate also polymerizes readily in emulsion, and under the proper conditions no difficulty is experienced in obtaining a smooth reaction requiring about 1 hour and giving a polymer of high intrinsic viscosity. Monomer purity is an important factor in controlling the reaction, and pure monomer requiring a small amount of catalyst is the easiest to control and gives the smoothest polymerization.

Polymerization of acrylic esters higher than n-propyl acrylate requires more of the emulsifying agent or a different emulsifying system. This might be expected in view of the properties of the

TABLE V. PREPARATION OF HIGHER ALKYL ACRYLATE POLYMERS AND COPOLYMERS

Experiment No.	Higher Acrylate	Ethyl Acrylate, %	Triton 720[a] %	Tergitol Penetrant No. 4[b] %	Acto 550-W[b], %	Triton R-100, %	Monomer in Emulsion, %	Initial Refluxing Temp., °C.	Ammonium Persulfate Used, %	Polymerization Time, Hours
E-125	n-Propyl	0	0.55	0.8	..	..	32	91	0.005	1.0
E-95	n-Butyl	0	1.0	0.75	..	..	33	95	0.006	1.5
M-198	n-Butyl	0	2.5	1.5	..	..	40	96	0.005	1.25
E-158	Amyl	0	0.5	1.5	..	..	33	98	0.010	1.25
M-153	Isopropoxyethyl	0	2.25	..	..	..	33	99	0.015	1.0
M-145	2-Ethylhexyl	0	6.2	..	1.0	..	40	98.5	0.021	2.0
M-143	2-Ethylhexyl	0	3.0	..	3.0	1.0	40	99.5	0.021	4.25
M-205	2-Ethylhexyl	0	2.5	1.5	..	..	40	98.5	0.021	1.33
E-128	n-Octyl	0	0.7	2.0	..	..	33	99	0.065	2.0
M-119	Capryl	0	5.0	..	..	..	40	99	0.150	1.5
M-121	Capryl	0	7.5	..	..	..	40	99	0.130	1.0
M-150	Capryl	0	5.5	..	1.0	..	40	99	0.083	1.75
M-158	Capryl	0	2.6	..	1.7	..	35	99	0.018	1.25
M-103	n-Butyl	80	2.0	..	2.0	1.0	40	83.5	0.005	2.5
M-104	n-Butyl	60	2.0	..	2.0	1.0	40	86	0.005	3.0
M-105	n-Butyl	40	2.0	..	2.0	1.0	40	88	0.005	1.75
M-210	n-Butyl	25	2.5	1.5	..	..	40	90	0.005	0.75
M-141	2-Ethylhexyl	50	2.0	..	2.0	1.0	40	88	0.007	3.0
M-144	2-Ethylhexyl	50	3.0	..	3.0	..	42	89	0.010	3.0
M-206	2-Ethylhexyl	25	2.5	1.5	..	..	40	93	0.011	1.5
M-358	2-Ethylhexyl	50	2.5	1.5	..	..	40	88	0.004	1.0
M-208	2-Ethylhexyl	75	2.0	..	2.0	1.0	40	84	0.004	2.0
M-82	Capryl	90	2.0	..	..	..	40	82	0.005	1.25
M-156	Capryl	50	3.75	..	..	..	40	87.5	0.010	0.75
M-155	Capryl	50	1.9	..	1.5	..	40	87	0.012	0.75
M-107	Capryl	65	2.5	..	2.0	0.5	40	86	0.005	2.0
M-291	Capryl	50	2.5	..	2.0	0.5	40	87	0.010	1.25
E-181	Tetrahydrofurfuryl	0	0.5	1.5	..	..	33	99	0.003	0.75

[a] Calculated as 28% emulsifying agent.
[b] Calculated as 50% emulsifying agent.

monomers and the polymers obtained (15, 16). The monomers are higher boiling and less water soluble, and have densities that become lower as the homologous series is ascended. The polymeric higher n-alkyl acrylates are softer and tackier than the lower esters, making the higher acrylic esters less suitable for emulsion polymerization under the conditions used with the lower esters. The higher refluxing temperatures increased the difficulty of making and maintaining a stable emulsion (the possibility of operating at reduced pressures to lower refluxing temperature was not investigated). When a water-soluble catalyst was used, additional emulsifier was needed for the solubilization or formation of micelles. The softer and tackier polymers were also harder to keep emulsified. In spite of these disadvantages, numerous polymers and copolymers of the higher n-alkyl acrylates were prepared.

All the emulsions described in Table V were good, although several preliminary experiments carried out to find improved emulsifying systems were relatively unsatisfactory. A water-soluble catalyst (ammonium persulfate) was used in an attempt to prepare polymers of high molecular weight because this catalyst had given polymeric ethyl acrylate of high molecular weight. Although use of benzoyl peroxide at lower temperatures was not investigated systematically, this catalyst might be useful for this type of emulsion. The addition of monomeric ethyl acrylate to the monomer mixture improved the polymerization characteristics. As little as 25% greatly facilitated polymerization and led to the production of a finer, more stable emulsion.

MISCELLANEOUS

A limited study of the use of organic peroxides was made to supplement the information previously reported (13) on benzoyl peroxide. Generally these catalysts (Table VI) were not so effective as ammonium persulfate—that is, a higher concentration was required to induce polymerization. Only diacetyl peroxide was effective in the same range of concentration as ammonium persulfate, but diacetyl peroxide required considerably more time. Acetylbenzoyl peroxide and succinic acid peroxide are active in promoting polymerization. The other catalysts were required in increased amounts and required much more time. Use of regulators and catalyst activators, such as ferricyanides (19), in conjunction with persulfate and peroxides will be discussed in another paper.

The continuous emulsion polymerization of acrylic esters appears advantageous because of the short reaction time, the high polymerization yield, and the relatively high boiling points of the monomers. Preparation of Lactoprene EV (95% ethyl acrylate, 5% 2-chloroethyl vinyl ether (11) by continuous emulsion polymerization was investigated briefly on a laboratory scale.

Ethyl acrylate from a storage vessel was pumped directly into a continuous steam distillation unit. The distilled monomer was separated from water automatically and continuously, and 5% chloroethyl vinyl ether was added before the mixture was pumped into the polymerization flask. The water, emulsifying agent, and catalyst were metered in simultaneously. The overflow from the first flask passed by gravity into a second polymerization flask and then into a third vessel, from which monomers were removed by steam distillation. The resin emulsion was siphoned continuously from the third flask to a receiving vessel. The yield of polymer was high.

To test the general utility of some of the emulsifying systems described here, other vinyl-type monomers were polymerized under conditions similar to those used with acrylic esters (Table VII). Styrene polymerized readily under reflux conditions and gave a good emulsion. More catalyst was used than with ethyl acrylate (about 40 times as much), but the time was held to less than 2 hours. Several copolymers of styrene were made with methyl acrylate and with butyl acrylate. Samples containing more than 1 mole of styrene for 1 mole of acrylate had discrete, solid, hard pieces (possibly polystyrene), which could be separated from the rest of the material.

Vinyl acetate also polymerized readily under the general conditions used with acrylic esters but required about eighty times as much catalyst as ethyl acrylate. Polymerization time was short,

TABLE VI. EFFECT OF VARIOUS CATALYSTS ON EMULSION POLYMERIZATION OF ETHYL ACRYLATE[a]

Experiment No.	Polymerization Initiator	%	Polymerization Time Hours
N-16	tert-Butyl perbenzoate	0.10	6.5
N-17	Di-tert-butyl peroxide	0.10	5.5
N-18	Di-tert-butyl diperphthalate	0.115	4.25
N-19	Acetyl benzoyl peroxide	0.02	2.0
N-20	Diacetyl peroxide	0.006[b]	2.75
N-21	Succinic acid peroxide	0.05	1.75
N-22	1-Hydroxycyclohexyl hydroperoxide	0.055	4.25

[a] Temperature range of all polymerizations 82° to 97° C.; small amount of polymer precipitated from each emulsion; 200 parts water, 2% Acto 550 W (dry basis), and 100 parts ethyl acrylate used for each emulsion.
[b] As 20% dimethyl phthalate solution.

TABLE VII. EMULSION POLYMERIZATION OF VARIOUS MONOMERS AND MONOMER MIXTURES

Experiment No.	Monomer Used	Methyl Acrylate, %	Butyl Acrylate, %	Triton 720a, %	Acto 550-Wb, %	Ammonium Persulfate, %	Total Solids, %	Initial Refluxing Temperature, °C	Polymerization Time, Hours	Remarks
M-147	Vinyl acetate	..	..	3	..	0.40	33	67	1.25	Small amount of precipitation
N-14	Styrene	..	..	3	..	0.20	33	93	1.75	Good emulsion
E-122c	Acrylonitrile	..	..	1	..	0.155	27	70	1.0	Emulsion precipitated completely during polymerization into fine particles
N-3	Styrene	90	..	..	1.5	0.02	33	74	2.0	Good emulsion
N-6	Styrene	80	..	..	1.5	0.03	33	74	1.5	Good emulsion
N-8	Styrene	70	..	..	1.5	0.03	33	74	2.0	Good emulsion
N-73	Styrene	50	..	..	2	0.008	43	72	4.0	Good emulsion
M-202	Styrene	45.4	..	..	2	0.007	43	81	1.0	Thick emulsion
N-74	Styrene	40	..	..	2	0.007	43	82	3.75	Thick emulsion
N-75d	Styrene	30	..	..	2	0.01	43	77	11.0	Good emulsion
N-78e	Styrene	..	55.2	2	..	0.015	33	95	1.5	Good emulsion
N-79e	Styrene	..	71	2	..	0.015	33	95	1.5	Good emulsion
N-114e	Styrene, 20% 2-Chloroallyl alcohol, 10%	70	..	..	1.8	0.023	43	78	3.25	Thick emulsion
N-40	Vinyl acetate	90	..	..	1.5	0.025	33	72	0.75	Precipitate, 1.26%
N-41	Vinyl acetate	80	..	..	1.5	0.01	33	70	1.25	Small amount of precipitation
M-148	Vinyl acetate, 90% 2-Chloroethyl vinyl ether, 10%	..	..	3	..	0.80	33	67	1.75	Small amount of precipitation
M-33f	n-Hexylmaleate, 30% Chloroethyl vinyl ether, 5% Ethyl acrylate, 65%	..	..	..	0.5	0.01	33	83	0.75	Good emulsion

a Calculated as 28% emulsifying agent.
b Calculated as 50% emulsifying agent.
c 4% Tergitol No. 4 also used.
d 1% Triton R-100 also used.
e 1% Tergitol No. 4 also used.
f 1.5% Tergitol No. 4 also used

and a good emulsion was obtained. Copolymers with ethyl acrylate were made in the usual manner.

Acrylonitrile separated out as a fine white powder during the polymerization. This powder was washed and dried and molded into a clear, slightly yellow, hard molding. Numerous copolymers of acrylonitrile and acrylates were made satisfactorily in the usual (12) manner.

Styrene and vinyl acetate were also copolymerized with chlorine-containing monomers (Table VII). The copolymers prepared in this manner presumably should be vulcanizable with the agents used in curing similar acrylic copolymers (11, 12).

Although the study of different vinyl monomers was brief, the results obtained suggest that the information obtained with acrylic esters should be generally useful in the emulsion polymerization of various other mono-olefinic vinyl monomers. Conditions (lower temperatures, higher pH, larger quantities of catalyst, and various additional agents) different from those described herein have been recommended (3, 18, 19) for the emulsion polymerization and copolymerization of butadiene and other dienes.

CONCLUSIONS

Relatively simple recipes and conditions were used satisfactorily to prepare several types of emulsion or dispersion containing acrylic resins of high molecular weight. The following recipes are recommended on the basis of the present study for the particular purposes mentioned:

For the general preparation of low-solids emulsions (45% or less of resin phase) and emulsions that can be coagulated without undue difficulty when the polymer is desired, recipe under "Experimental."

Emulsions having high solids content (45 to 60%) or unusual stability to electrolytes, recipe M-94, Table III.

Emulsions that, upon evaporation of water, deposit clear and almost colorless films, recipe M-330, Table II.

Emulsions that yield vulcanizable (11, 12) films, any satisfactory emulsion in which 5% or more of a monomer such as chloroethyl vinyl ether or isoprene, is used in the monomer mixture.

Conditions described in the present paper differ from those recommended for dienes (19), in that the acrylate polymerizations are characterized by higher temperatures, less time, less catalyst or initiator, pH of approximately 7 or lower, use of synthetic surface active agents instead of soaps, high conversions, and absence of regulators and catalyst activators such as mercaptans and

ferricyanide, respectively. Conditions used with acrylic esters were satisfactory for the polymerization of several other mono-olefinic vinyl-type monomers.

Acrylic resins prepared with small amounts of persulfate or peroxides—i.e., those recommended in the present work—were readily soluble in several organic solvents, whereas the larger proportion of polymerization catalyst recommended for dienes caused the formation of insoluble polymers.

Emulsion polymerization of acrylic esters in media of high pH was accompanied by some saponification, whereas hydrolysis was negligible when the pH was approximately 7. Presumably other monomeric esters, such as vinyl esters, maleates, and fumarates, would behave similarly.

LITERATURE CITED

(1) Barron, H., British Plastics, 11, 467 (1940).
(2) Bennett, H., ed., "Emulsion Technology," Brooklyn, Chemical Publishing Co., 1946.
(3) Chittenden, F. D., McCleary, C. D., and Smith, H. S., "High Solids Synthetic Latex Directly from the Reactor," presented before the Division of Rubber Chemistry at the 109th meeting of the AM. CHEM. SOC. in Atlantic City, N. J.
(4) Clayton, W., "Theory of Emulsions," 4th ed., p. 199, Philadelphia, Blakiston & Co., 1943.
(5) Codd, L. W., and Hamblin, F. T., U. S. Patent 2,299,128 (Oct. 20, 1942).
(6) Cupples, H. L., U. S. Dept. Agriculture, Bureau of Entomology and Plant Quarantine, E-607 (1943).
(7) Duncan, R. A., IND. ENG. CHEM., 26, 24 (1934).
(8) Frank, R. L., and Adams, C. E., J. Am. Chem. Soc., 18, 908 (1946).
(9) Goldsmith, H. A., Chem. Inds., 52, 326 (1943).
(10) Koningsberger, C., and Saloman, G., Rubber Chem. and Technol., 19 (4), 1029 (1946).
(11) Mast, W. C., and Fisher, C. H., IND. ENG. CHEM., 40, 107 (1948).
(12) Mast, W. C., Rehberg, C. E., Dietz, T. J., and Fisher, C. H., Ibid., 36, 1022 (1944).
(13) Mast, W. C., Smith, L. T., and Fisher, C. H., Ibid., 37, 365 (1945).

(14) Ratchford, W. P., and Faucette, W. A., unpublished work.

(15) Rehberg, C. E., and Fisher, C. H., *J. Am. Chem. Soc.*, 66, 1203 (1944).

(16) Rehberg, C. E., and Fisher, C. H., "Properties of Monomeric and Polymeric Acrylates and Methacrylates," presented before the Division of Paint, Varnish, and Plastics Chemistry, at the 109th meeting of the Am. Chem. Soc., Atlantic City, N. J.

(17) Renfrew, A., and Gates, W. E. F., U. S. Patent 2,296,403 (Sept. 22, 1942).

(18) Semon, W. L., *Chem. Eng. News*, 24, 2900 (1946).

(19) Starkweather, H. W., Bare, P. O., Carter, A. S., Hill, F. B., Jr., Hurka, V. R., Mighton, C. J., Sanders, P. A., Walker, H. W., and Youker, M. A., Ind. Eng. Chem., 39, 210 (1947).

(20) Sutheim, G. M., "Introduction to Emulsions," p. 55, Brooklyn, Chemical Publishing Co., 1946.

(21) Thorpe, J. F., "Dictionary of Applied Chemistry," 4th ed Vol. IV, pp. 284-303, London, Longmans, Green and Co., 194

(22) Van Antwerpen, F. J., Ind. Eng. Chem., 35, 126 (1943).

(23) Williams, T., and Sudborough, J. J., *J. Chem. Soc.*, 101, 412 (1912).